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Abstract of **GB1473161**

1473161 Coated products NIPPON PAINT CO Ltd 9 July 1974 30324/74 Heading B2E [Also in Division C7] A conductive material, e.g. Fe, Cu, Zn, Al or material made conductive by coating with conductive material or by adding thereto metal powder or graphite filler, is coated by applying thereto (1) an inorganic coating layer at least 10 Å thick containing a silicic acid base material e.g. an alkali metal (Li, Na, K) silicate, a quaternary ammonium silic- ate, colloidal silica and/or a modified silicate, and/or a metal phosphate e.g. a monobasic phosphate of a di- or poly-valent metal (Mg, Zn, Al, Ca), a sesqui, secondary or tertiary salt of a metal phosphate, a polyphosphate and/or calcined metal phosphate, then (2) an organic coating layer by electrophoretic de- position. The electrodepositable composition may be (a) anionic comprising a resin con- sisting of a reaction product of an aliphatic ester and an α, #-unsaturated dicarboxylic acid or its anhydride, with or without a polyol, a mixed resin comprising a copoly- mer resin having carboxyl groups or an alkyd resin and an amine-aldehyde condensation product, the resin being neutralized with an organic or inorganic base, or (b) cationic comprising a resin consisting of a reaction product of an epoxy compound with an amine salt, or containing a quaternary amine salt residue. The inorganic coating material may be mixed with a colouring pigment, e.g. TiO 2 , red iron oxide, clay or talc, a surface active agent, a hardening accelerator, e.g. a SiF 6 , SiB 4 or metal oxide, or an organic resin, and applied by spray coating, brushing, dipping or electrodeposition, then dried or baked.

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(54) METHOD FOR COATING A CONDUCTIVE MATERIAL INVOLVING ELECTROPHORETIC DEPOSITION

(71) We, NIPPON PAINT CO. LTD., a corporation organised under the laws of Japan, of No. 1—1 Oyodo-cho Kita 2-chome, Oyodo-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of coating a conductive material which involves electrophoretic deposition. More particularly, the invention is concerned with a method of coating a conductive material which comprises applying an inorganic paint composition to a conductive material, and thereafter applying thereto a conventional electrodeposition coating.

Paints in which the base material mainly comprises a resin have been widely proposed as coating compositions, and various such paints and corresponding coating methods have been proposed in accordance with the various uses. On the other hand, inorganic paint compositions have been proposed with favourable properties such as incombustibility, heat resistance or hardness not given by the organic paints. Thus, the organic paints have weak heat resistance, but on the other hand, the inorganic paints are brittle and have a remarkably inferior flexibility and impact strength. Accordingly, it has been proposed to laminate the organic coating layer with the inorganic coating layer so as to combine both characteristics. However, such a method has not been practically used because, when the inorganic and organic coating layers are laminated together by a conventional method, the adhesion is not sufficient.

We have therefore sought to discover an improved method of obtaining a laminated coating layer having both the good durability properties of an inorganic coating layer and the flexibility of an organic coating layer.

Generally, it is considered difficult to apply an electrodeposition coating to a coating layer formed on a conductive material, but, according to the present invention, we have found that an electrodeposition coating can be applied to an inorganic coating layer with a thickness of 50 μ or more, and further that the composite coating layer of the inorganic and organic coating layers obtained by such a method has excellent adhesion which could not be obtained by a conventional spray coating or brushing.

The present invention provides a method of coating a conductive material which comprises applying thereo, other than by electrophoresis, an inorganic composition containing at least one of a silicic acid base material and a metal phosphate to form an inorganic coating layer with a thickness of at least 2—3 μ, and preferably at least 5—6 μ, and then applying thereto an electrodepositable composition by electrophoretic coating to form an organic coating layer on the inorganic coating layer. A range of thickness of 5—10 μ, preferably 6—8 μ, may be used for the first coating step, and greater thicknesses of from 10—30 μ or even from 30 μ to 180 μ, in particular at least 50 μ may be used. However, thicknesses of 3 to 5 μ and 6 to 8 μ represent practical operating ranges.

Although it is well known that an electrodeposition coating may be applied to a coating film which is made electroconductive, the electrodeposition coating in the present invention is based on an entirely different principle from that of the conventional electrodeposition coating method because the relatively thick inorganic coating layer is substantially not electroconductive in itself. In general, an organic coating layer is non-conductive and therefore the electrodeposition coating cannot be applied thereto. On the other hand, an inorganic coating layer is more porous and

hydrophilic than an organic coating layer, and, therefore, when it is dipped in a water-soluble electrodepositable paint composition, water penetrates into the inorganic coating layer, and, as a result, electricity can be passed through the inorganic coating layer. This is the principle of the present electrodeposition coating.

When an inorganic coating layer is hardened at a comparatively low temperature without melting, it is generally more porous than an organic coating layer, and, therefore, even if the starting material for the inorganic coating has an anticorrosive property, the inorganic coating layer does not have enough corrosion resistance and rust frequently occurs when it is tested by a salt spraying test. In contrast, the composite coating layer obtained by the present method has excellent corrosion resistance according to the synergistic effect of the inorganic coating layer and the organic coating layer.

The inorganic composition used in the present invention contains at least one of a silicic acid base material and a metal phosphate as the base. The preferred examples of the silicic acid base material are an alkali metal silicate, a quaternary ammonium silicate, a colloidal silica, a modified silicate which is obtained by modifying an alkali metal silicate with a metal ion, or any mixture thereof. 4.0:1. The quaternary ammonium silicate may be used, e.g., lithium silicate with a molar ratio of SiO_2 to Li_2O of 3.5:1 to 20:1, sodium silicate with a molar ratio of SiO_2 to Na_2O of 1.5:1 to 4.0:1 or potassium silicate with a molar ratio of SiO_2 to K_2O of 1.5:1 to 4.0:1. The quaternary ammonium silicate may be prepared, for example, by passing an aqueous solution of an alkali metal silicate and a water-soluble amine through an ion-exchange resin. The colloidal silica is a colloidal silica sol stabilized with an acid or an alkali. These silicic acid base materials may be used alone or in a mixture of two or more kinds thereof.

The metal phosphate used in the present invention includes a monobasic phosphate of a di- or poly-valent metal, such as monobasic magnesium phosphate, monobasic zinc phosphate, monobasic calcium phosphate or monobasic aluminium phosphate or any mixture thereof; a sesqui, secondary or tertiary salt of a metal phosphate preferably the metal phosphate as mentioned above; a polyphosphate which can be prepared by heat treatment of the metal phosphate as mentioned above; or a conventional calcined metal phosphate; or any mixture thereof. The polyphosphate is preferably prepared by heating a monobasic metal phosphate at 150 to 900°C. The polyphosphate is usually not a single compound but a mixed composition, and, therefore, the chemical structure thereof is indefinite, but according to X-ray diffraction, some polyphosphates have a peculiar diffraction angle. Commercial polyphosphate products include HB Hardner (trade mark of Farbwerke Hoechst A.G.) and K-substance (made by Teikoku Kako K.K.). Silica Phosphate (Corrosinon SPO—28, trade name of Mizasawa Chemical Co.) is an example of a commercial calcined metal phosphate product.

The silicic acid base material and the metal phosphate may be used alone or in various combinations as the base. Preferred examples of the combination include mixtures of acid colloidal silica and a monobasic metal phosphate, and mixtures of a cyclic polyphosphate and an alkali metal silicate.

The inorganic material as above-listed or a mixture of two or more kinds thereof is optionally mixed with a conventional colouring pigment or loading pigment (e.g. titanium dioxide, red iron oxide, clay or talc), and then dispersed by a conventional method using a ball mill or high speed agitator to give the desired inorganic composition. A surface-active agent, a hardening accelerator, or an organic resin may be optionally added to the inorganic composition. The hardening accelerator may be, for example, a silicofluoride, a silicoborate or a metal oxide.

The electrodepositable composition used in the present invention includes various conventional compositions, and may in general be classified as an anionic electrodepositable composition or a cationic electrodepositable composition.

The resin used for the anionic composition may be, for example, a reaction product of an aliphatic ester and an α,β-unsaturated dicarboxylic acid or its anhydride. The aliphatic ester may be, for example, a derivative of a drying oil, a semi-drying oil or a tall oil, for example, a modified aliphatic ester resin incorporated with an unsaturated monomer (e.g. styrene, butadiene, vinyltoluene or methyl methacrylate); an alkyd resin prepared from a drying or semi-drying oil; an ester of an epoxy compound (e.g. Epikote 828, Epikote 1001, or Epikote 1004; each being a trade mark of Shell International Research Mant.) with an aliphatic acid (e.g. linseed oil fatty acid, Chinese tung oil fatty acid, cotton seed oil fatty acid, dehydrated castor oil fatty acid, or tall oil fatty acid) or an ester of a polyol compounds (e.g. ethylene glycol, 1,2-propylene glycol, 1,4-butanediol, diethylene glycol, neopentyl glycol, or trimethylolpropane) or a resinous polyol (e.g. an allyl alcohol homopolymer, or a copolymer of allyl alcohol with an ethylenically unsaturated monomer such as styrene) with an aliphatic acid. The aliphatic ester is reacted with an α,β-unsaturated dicarboxylic acid or its anhydride (e.g. maleic acid, maleic anhydride, itaconic acid, or itaconic anhydride) to give the desired resin.

Other suitable resins may be prepared by

reacting the reaction product of an aliphatic ester and an α,β-unsaturated dicarboxylic acid or its anhydride as mentioned above with a polyol (e.g. ethylene glycol, diethylene glycol, 2,2-bis-(4-hydroxycyclohexyl)-propane or trimethylolpropane), or by reacting a resinous material having a hydroxy group or oxirane ring (e.g. an allyl alcohol-styrene copolymer having a molecular weight of 500 to 5,000, glycidyl methacrylate, or methyl methacrylate-*n*-butyl acrylate copolymer), with an aliphatic acid (e.g. linseed oil fatty acid, Chinese tung oil fatty acid, cotton seed oil fatty acid, dehydrated castor oil fatty acid, or tall oil fatty acid) and then reacting the remaining hydroxy group with an unsaturated dicarboxylic acid or its anhydride (e.g. maleic acid, maleic anhydride, itaconic acid or itaconic anhydride). A further useful resin may be a mixed resin composition which comprises a copolymer resin having carboxyl groups, e.g., comprising a hydroxyalkyl ester of an unsaturated carboxylic acid (e.g. 2-hydroxyethyl methacrylate or 2-hydroxy-*n*-propyl acrylate), an unsaturated carboxylic acid (e.g. acrylic acid or methacrylic acid), and an ethylenically unsaturated monomer (e.g. styrene, vinyltoluene, ethyl acrylate, *n*-butyl acrylate, methyl methacrylate, *n*-butyl methacrylate, acrylonitrile or vinyl acetate), and an amine-aldehyde condensation product. The amine-aldehyde condensation product includes a condensation product of formalin with melamine, benzoguanamine or urea, or an analogous product, which is preferably etherified with an alcohol. Moreover, there may be used a mixed resin comprising an alkyd resin having a comparatively high acid value (i.e. of at least 50) and the amine-aldehyde condensation product.

For the preparation of the anionic electrodepositable composition from the above-listed resins, the resin may be first made water-soluble by neutralizing the carboxyl groups contained therein. The neutralizing agent therefor may be an inorganic base such as potassium hydroxide or ammonia, or an organic base such as an amine (e.g. methylamine, ethylamine, dimethylamine, triethylamine, morpholine, ethanolamine, methylethanolamine or ethylenetriamine), which may be used alone or in a mixture thereof. After neutralizing the resin, various pigments or dispersing agents may optionally be added to the resulting mixture, and the mixture thus obtained is then diluted with tap water or deionized water to give the desired electrodepositable composition.

The electrodepositable vehicle, i.e., the resin used for the preparation of the anionic composition may contain a mineral acid (e.g. phosphoric acid or sulphonic acid) as well as the above carboxylic acid.

The resin used for the cationic electrodepositable composition may also be a cationic resin material which is solubilized by an acid, for example, a reaction product of an epoxy compound (e.g. Epikote (trade mark) 836, trade name of Shell International Research Mant.) with an amine salt (e.g. a reaction product of an alcohol amine, lactic acid, boric acid and glycol) as disclosed in Japanese Patent Laid Open Publication No. 13432/1972. There may also be used a resin containing a quaternary amine salt residue (e.g. a solution of a copolymer of aminoethyl methacrylate and an ethylenically unsaturated monomer which is neutralized with acetic acid). These resins may be admixed with pigments and various other additives in the same way as the anionic composition to give the desired electrodepositable composition.

The conductive substrate to be coated by the present method may be a material which is conductive *per se*, such as a metal (e.g. iron, copper, zinc or aluminium), or a top-coated metal, or a material which has been made electrically conductive by coating a non-conductive substrate with a metal or other conductive material, e.g. through plating or deposition, or by adding a filler such as a metal powder or graphite.

According to the present method, the inorganic composition mentioned above is applied to the conductive material to be coated by a coating method such as spray coating, brushing, dipping or electrodeposition coating, and drying at room temperature or baking to form an inorganic coating layer. The coated substrate having the inorganic coating layer is then dipped in a bath containing the electrodepositable composition mentioned above. When an anionic composition is used, the substrate is employed as the anode, and when a cationic composition is used, the substrate is employed as the cathode. Electric current is passed at an applied voltage of 10 to 500 volts for 1 second to 10 minutes to form an organic coating layer.

In the electrodeposition process, the inorganic coating layer may have water resistance so that it is not damaged during the electrodeposition process. The substrate coated by the electrodeposition is then dried as it is or preferably after rinsing with water.

As described hereinbefore, when the organic coating layer is applied to the inorganic coating layer, or the inorganic coating layer is applied to the organic layer by the usual method, the adhesion between the both layers is generally not enough, but according to the present method, the product has excellent adhesion. According to the microscopic investigation, the electrodeposited organic coating layer has been tightly applied to the uneven surface and to the pores of the inorganic coating layer which shows a sufficient anchoring effect to give the desired composite coating layer.

According to the present invention, there

can be obtained a composite coating layer having the advantageous properties mentioned below as a result of the combination of the inorganic coating layer and the electrodeposition coating layer.

(1) The present composite coating layer has superior corrosion resistance to that obtained by the conventional electrodeposition coating which is applied to a steel panel subjected to chemical treatment with zinc phosphate, because it shows both a rust inhibitory effect owing to the starting material of the inorganic composition, i.e. the silicic acid base material and the metal phosphate, and excellent adhesion of the electrodeposition coating.

(2) The usual defect of the inorganic coating layer, i.e. its brittleness, is covered by the electrodeposition coating and thereby the composite coating layer has improved impact strength and flexibility.

(3) The conventional electrodeposition has the defect that, when the substrate to be coated is a metal, particularly iron, the iron ion is eluted out onto the electrodeposition coating, which results in colouring of the coating layer. On the other hand, according to the present invention, the amount of the eluted iron ion is extremely low in comparison with that obtained by the conventional electrodeposition coating which is applied to a steel panel subjected to chemical treatment with zinc phosphate. Thus, the present method can give a purely white coating layer without the defect of colouring and having excellent corrosion resistance even in the case of a white-coloured electrodeposition coating.

(4) Since the inorganic coating layer has excellent heat resistance and incombustibility, even after the upper organic coating layer (electrodeposition coating layer) is destroyed under severe heat conditions, the substrate is still protected by the lower inorganic coating layer.

(5) The present product may be optionally topcoated by various conventional paints, and thereby a product having a good coating appearance can be obtained.

(6) The inorganic composition and the electrodepositable composition used in the present invention are a cold water paint, and therefore the present product is favourable from the viewpoints of safety and the prevention of pollution.

The present invention is illustrated by the following Examples but not limited thereto. In the Examples "part" means part by weight.

Example 1.

Inorganic Composition [A]:

Sodium silicate (Grade number: 3)	70 parts
Lithium polysilicate (48 (made by DuPont)	30 parts
Titanium dioxide	30 parts
Kaolin	106 parts
Demol N (trade mark of Kao Soap Co.)	2 parts
Water	120 parts

The above components are dispersed by ball mill for 15 hours to give the desired inorganic composition.

Electrodepositable Composition [B]:

Anhydrous trimellitic acid	32 parts
Propylene glycol	30 parts
Adipic acid	8 parts

The above components are reacted at 170°C so that the acid value becomes 65, tall oil aliphatic acid (30 parts) is added and the mixture is further reacted so that the acid value becomes 55. Isobutanol (20 parts) is added to the reaction mixture and the mixture is then neutralized with triethylamine (12 parts). Red iron oxide (35 parts) is suspended in the resin thus obtained, and the resulting mixture is diluted with water (1,000 parts) to give the desired electrodepositable composition.

After controlling the viscosity of the Inorganic Composition [A] by adding water (viscosity: 2 poise), the inorganic composition is applied by dipping to a mild steel panel which is degreased and treated with sandpaper to make the surface rough so that the thickness of the coating layer becomes about 30 μ in the dry state, and the product is then dried by baking at 160°C for 15 minutes. The coated panel is dipped in Electrodepositable Composition [B], and then coated therewith by passing electric current at 200 volts for 3 minutes the coated panel being used as the anode. The resulting panel is rinsed with water and then cured by baking at 170°C for 30 minutes. The composite coating layer thus obtained has a thickness of about 50 μ and the intercoat adhesion is very good.

As Comparative Example 1, a commercial melamine-alkyd paint is applied and baked on to a mild steel panel coated with Inorganic Composition [A]. The melamine-alkyd paint is prepared by dispersing Alkyd Resin Becka-

sol (trade mark) J 524 (made by Dainippon Ink & Chemicals Inc.; 50 parts), melamine resin (Super Beckamine G 821, trade mark of Dainippon Ink & Chemicals Inc.; 17 parts), titanium dioxide (27 parts), *n*-butyl alcohol (5 parts) and xylene (20 parts). The adhesion between the layers of the product thus obtained is inferior and the second (upper) coating layer crazes and is stripped.

The properties of the coating layer in the products of the Example 1 above are also compared with those of the coating layer obtained by coating Electrodepositable Composition [B] and the melamine-alkyd paint in a total thickness of about 50 μ (Comparative Example 2). The results are shown in Table 1 as follows.

TABLE 1

Name of the test	Method for the test		The product of Example 1	The product of Comparative Example 2
Folding test	Folded at right angle (Diameter: 10mm)		Fine cracking No peeling of the coating layer	Cracking
Impact test	DuPont method (Diameter: 1/2 inch)	300g × 50cm	Good	Cracking
		500g × 30cm	Good	Cracking
Salt spray test	Tested by using Salt spray tester for 500 hours Test piece is crosscut		Good No rust on the cut part No lowering of adhesion	Cut part is rusted in 5mm in width Adhesion lowers
Salt soak test	Test piece is soaked in 3% saline solution for 1 month Test piece is crosscut		Good No rust on the cut part No lowering of adhesion	Cut part is rusted and deep erosion is observed Blistering Lowering of adhesion particularly around the cut part
Warm water soak test	Test piece is soaked in tap water of 40°C for 1 month		A little blushing of the coating layer No blistering	Blistering
Flame resistance test	Test piece is exposed on the flame of gas burner for 30 minutes		Inorganic coating layer is remained	Coating layer completely disappears

Example 2.

Inorganic composition [C]:

30% aqueous solution of potassium silicate having a molar ratio of SiO_2:K_2O being 3.5	80 parts
Colloidal silica (Snowtex 30, trade mark of Nissan Chemical Industries Ltd.)	20 parts
Red iron oxide	10 parts
Talc	60 parts
Water	50 parts

The above components are dispersed in the same manner as in Example 1, and a paste prepared by dispersing sodium silicofluoride (40 parts) in water (60 parts) is added (5 parts) to give the desired inorganic composition.

Electrodepositable composition [D]:

A mixture of an epoxy resin (Epikote 836, trade mark of Shell International Research Mant.; 200 parts), methanol (55 parts), stannous chloride (2.5 parts) and diethylene glycol (28 parts) is reacted at 150°C for 3 hours to give a product [X]. Separately, a mixture of N,N-dimethylethanolamine (742 parts), lactic acid (714 parts) and toluene (300 parts) is subjected to a dehydration reaction at 110°C for 4 hours and boron oxide (245 parts) and neopentyl glycol (728 parts) are added to the reaction mixture. The mixture is further subjected to dehydration at 120°C for 4 hours to give a product [Y]. The product [Y] (13 parts) is added to the product [X] (200 parts) at 70°C over a period of 30 minutes with agitation. Formic acid and deionized water (1900 parts) are added to the resulting solution to regulate the pH value to 4.5, and a paste prepared by dispersing titanium dioxide (100 parts) in melamine resin (Cymel 300, trade mark of Union Carbide Corp.; 40 parts) and water (60 parts) is further added to give the desired electrodepositable composition.

Inorganic Composition [C] is applied to a stainless steel panel, an aluminium panel and a galvanized mild steel panel by using an electrostatic spraying machine (Nakaya type) so that the thickness of the coating layer becomes 10 μ in the dry state, and the product is then dried at 120°C for 10 minutes. Each coated panel is subjected to an electrodeposition coating with Electrodepositable Composition [D] at 200 volts for 2 minutes, the coated panel being used as the anode, and then the resulting panel is baked at 180°C for 20 minutes to give a composite coating layer having a thickness of about 30 μ and a smooth surface. All coated panels, i.e. the stainless steel panel, the aluminium panel and the galvanized mild steel panel have excellent inter-coat adhesion.

As Comparative Examples 3 and 4, the panels coated with Inorganic Composition [C] are also coated with an acrylic resin paint comprising an acrylic resin (Rustrazole A 405, trade mark of Dainippon Ink & Chemicals Inc.; 35 parts), a melamine resin (Super Beckamine G 820, trade mark of Dainippon Ink & Chemicals Inc.; 16 parts), titanium dioxide (25 parts), xylene (25 parts), butyl alcohol (5 parts) and butyl acetate (5 parts) by baking, or with an epoxy enamel paint which is prepared by mixing a paste comprising an epoxy resin (Epikote 1001, trade mark of Shell International Research Mant.; 22 parts), titanium dioxide (28 parts), xylene (15 parts), methyl isobutyl ketone (5 parts) and ethyl Cellosolve (trade mark) (7 parts) with an amide resin (Lacquamide ODG—44, trade mark of Dainippon Ink & Chemicals Inc.; 9 parts), and then dried. The composite coating layers have inferior adhesion and are peeled off by a peeling test using Scotch (trade mark) brand Cellophane (trade mark) tape.

The properties of the coating layer in the products of the above Example 2 obtained by coating a galvanized mild steel panel and an aluminium panel are compared with those of the coating layer in the products (thickness of the coating layer: about 30 μ), which are obtained by applying a thermosetting type acrylic paint crosslinked with a melamine to a galvanized mild steel panel (Comparative Example 5) and an aluminium panel (Comparative Example 6), which are first coated with Electrodepositable Composition [D]. The results are shown in Table 2 as follows.

TABLE 2

Name of the test	Method for the test		Galvanized mild steel panel: The product of Example 2	Galvanized mild steel panel: The product of Comparative Example 5	Aluminium panel: The product of Example 2	Aluminium panel: The product of Comparative Example 6
Folding test	In the same manner as in Example 1		Fine cracking	Cracking	Fine cracking	Cracking
Impact test	DuPont method (Diameter: 1/2 inch)	300g × 50cm	Good	Dry spot of the coating layer	Good	Cracking
		500g × 30cm	Cracking	Many cracking	Cracking	—
Salt spray test	In the same manner as in Example 1		Good Rust on the cut part	Blistering and rust along the cut part	Good	Blistering of all part
Salt soak test	In the same manner as in Example 1		Good	Blistering	Good	Much blistering
Flame resistance test	In the same manner as in Example 1		Inorganic coating layer is remained	Coating layer disappears	Inorganic coating layer is remained	Coating layer disappears

Example 3.

Inorganic Composition [E]:

The Inorganic Composition [C] (100 parts) used in Example 2 is admixed with a resin emulsion (Nikasol A—08, trade mark of Nippon Carbide Industries Co., Inc.; 3 parts) to give the desired Inorganic Composition [E].

Inorganic Composition [E] is applied to a degreased steel panel by an electrostatic spraying machine (Nakaya type) so that the thickness of the coating layer becomes 10 μ in the dry state, and the product is then dried at 120°C for 10 minutes. Electrodepositable Composition [D] is applied to the coating panel in the same manner as in Example 2,

and the resulting panel is dried at 180°C for 20 minutes to give a composite coating layer having a thickness of about 30 μ.

The properties of the coating layer of the product thus obtained are compared with those of the product (Comparative Example 7), which is produced by applying Inorganic Composition [C] and Electrodepositable Composition [D] to a degreased steel panel in the same manner as in Example 2. The results are shown in Table 3.

TABLE 3

Name of the test	Method for the test	The product of Example 3	The product of Comparative Example 7
Folding test	In the same manner as in Example 1	Good	Fine cracking
Impact test	DuPont method (Diameter: 1/2 inch) 500g x 50cm	Good	Cracking
Salt spray test	In the same manner as in Example 1	Good	Good

As made clear from the above results, the properties of the composite coating layer, e.g. the flexibility can be improved by admixing a small amount of an organic resin.

Example 4.

Inorganic Composition [F].

A lithium silicate (Lithium Silicate 75, made by Nissan Chemical Industries, Ltd.; 70 parts), a colloidal silica (Snowtex 20, trade mark of Nissan Chemical Industries Ltd.; 30 parts) and water (100 parts) are mixed to give the desired inorganic composition.

Electrodepositable Composition [G].

A mixture of methyl methacrylate (30 parts), ethyl acrylate (25 parts), *n*-butyl acrylate (30 parts), 2-hydroxy-n-propyl acrylate (10 parts), methacrylic acid (6 parts) and benzoyl peroxide (1 part) is added dropwise to a mixed solvent of butyl Cellosolve (trade mark) (30 parts) and *n*-butyl alcohol (20 parts) at 130°C over a period of 4 hours to give a resinous product. The product (61 parts) is partially neutralized by adding deionized water (75 parts) and diethylamine (2 parts), a melamine resin (Cymel 300, trade mark of Monsanto Chemicals Ltd.; 21 parts), dieionized water (18 parts) and diethylamine (7 parts) are added, and the resulting mixture is diluted with deionized water so that the nonvolatile solid content becomes 12% by weight to give the desired electrodepositable composition.

A mile steel panel which has been degreased and treated with sandpaper to make the surface rough is dipped in Inorganic Composition [F], the steel panel being used as the cathode and is then coated therewith by passing electric current at 10 volts for 10 seconds, so that the inorganic composition is coated to a thickness of 2 to 3 μ in the dry state. After rinsing with water, the coated panel thus obtained is dipped in Electrodepositable Composition [G] with the steel panel being used as the cathode, and is then electrophoretically coated therewith by passing electric current at 80 volts for 3 minutes. The resulting panel is rinsed with water and is then baked at 190°C for 20 minutes to give a composite coating layer having a thickness of 20 μ (in the dry state).

The properties of the coating layer of the product obtained above are compared with those of the product having a thickness of 20 μ (in the dry state; Comparative Example 8) which is produced by electrodeposition coating the same mild steel panel as used above with Electrodepositable Composition [G] only. The results are shown in Table 4.